

## The effect of lithium insertion on the structure of tin oxide-based glasses

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### Abstract

Two different SnO-based glasses,  $\text{Sn}_2\text{B}_3\text{O}_{6.5}$  and  $\text{Sn}_2\text{B}_2\text{AlO}_{6.5}$ , have been examined with FT-IR and Raman spectroscopy at different stages during the first electrochemical cycle. It was found that some disruption of the connection between borate units in the network occurred during cycling. There was also an irreversible formation of  $\text{Li}_3\text{BO}_3$  that can be related to the large capacity loss. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Tin-based amorphous composite oxides have recently received much attention as the active component in anode materials for rechargeable lithium ion batteries [1]. These materials show an outstanding performance in terms of reversible Li-storage capacity (>600 mAh/g). However, a large irreversible capacity loss occurs during the first cycle. The reaction underlying this loss is believed to be the formation of metallic tin, whereby the lithium ions, when inserted into the material, react with oxygen in the tin oxide [2].

New results indicate the importance of the constituents of the glass network and also the significance of the role of oxygen for good cycleability [3–6]. The effect of the glass network on cycleability is not yet clear, but, by substituting different components of the network, it should be possible to lower the irreversible capacity. We have investigated the behaviour of two different SnO-based glasses,  $\text{Sn}_2\text{B}_3\text{O}_{6.5}$  and  $\text{Sn}_2\text{B}_2\text{AlO}_{6.5}$ , during the first electrochemical cycle. The cycling was interrupted at certain stages and the electrodes were examined with micro-Raman and infrared spectroscopy.

### 2. Experimental

The glasses used in this work were prepared using standard melt-quenching techniques. The electrode preparation followed by half-cell  $(\text{Li} \mid \text{liq. electrolyte} \mid \text{Sn-glass})$  assembly and cycling have been described thoroughly, elsewhere [7]. Prior to the vibrational spectroscopy measurements, the electrodes were allowed to reach electrochemical equilibrium and then washed with DMC and vacuum dried at room temperature to remove the remains of the electrolyte.

The diffuse reflectance infrared (DR-IR) spectra were measured using a Bruker IFS 66v/S FT-IR spectrometer equipped with a DTGS detector using a diffuse reflectance device (Graseby Specac, mod. Selector). The confocal micro-Raman experiments were performed on a DILOR XY800 spectrometer. The 514.5 nm line from an Ar-ion laser was used as the excitation source.

### 3. Results and discussion

The electrodes were examined at four different stages of the first cycle: before cycling, at 0.4, 0.01 and at 2.5 V. The cycling behaviour is comparable to that reported for other SnO-based glasses [5,6]. The infrared and Raman results are shown in Figs. 1 and 2, respectively. The two compounds do show similar general trends.

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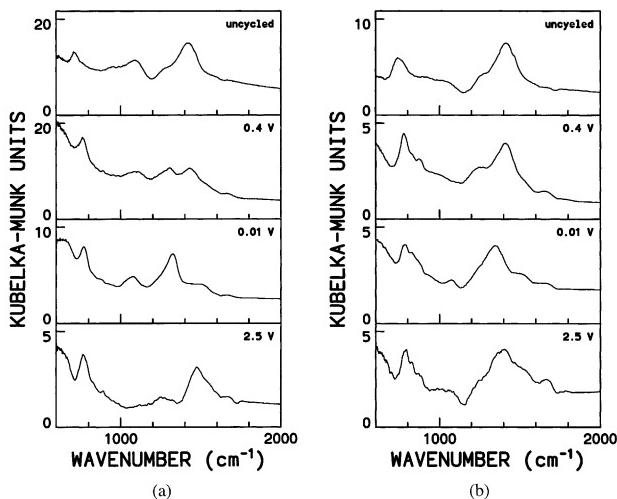


Fig. 1. DR-IR spectra for the (a)  $\text{Sn}_2\text{B}_3\text{O}_{6.5}$ , and (b)  $\text{Sn}_2\text{B}_2\text{AlO}_{6.5}$  electrodes.

Comparing the DR-IR spectra at 0.4 V with those for the uncycled samples, an irreversible shift from 705 to 760  $\text{cm}^{-1}$  is present. This band is attributed to bending of the B–O–B bonds [8]. The increase in frequency of this mode is associated with the presence of non-bonding oxygen. During the rest of the first cycle a reversible shift of the bands at around 1400  $\text{cm}^{-1}$  occurs. These vibrations are attributed to B–O stretching vibrations of the differently connected  $\text{BO}_3$  units. The major difference in the DR-IR spectra for the two compounds is related to the broad contributions in the region 850–1200  $\text{cm}^{-1}$ , which is attributed to the presence of  $\text{BO}_4$  units. An irreversible decrease of these species is observed in the case of tin–borate glass, while a more stable presence is evidenced for the tin–borate–aluminate.

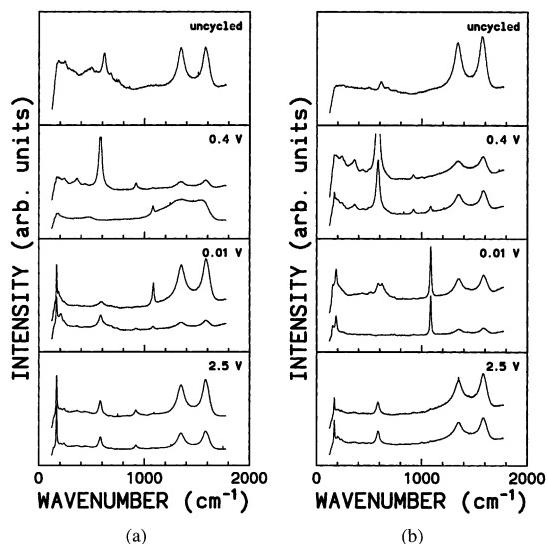


Fig. 2. Raman spectra for the (a)  $\text{Sn}_2\text{B}_3\text{O}_{6.5}$ , and (b)  $\text{Sn}_2\text{B}_2\text{AlO}_{6.5}$  electrodes.

The Raman spectra present two peaks at about 1350 and 1600  $\text{cm}^{-1}$  due to carbon black, and one peak around 600  $\text{cm}^{-1}$  due to  $\text{SnO}_x$  (see Fig. 2). Only smaller features are associated with contributions from the glass. Peaks at 920 and 1090  $\text{cm}^{-1}$  are observed in the spectra of the 0.4 V samples, which are not present in the spectra of the uncycled electrodes. These bands evolve in different ways during cycling however. The 920  $\text{cm}^{-1}$  band has an irreversible character and is attributed to the presence of orthoborate [8], whereas the 1090  $\text{cm}^{-1}$  band, associated with the presence of Li–O co-ordination, appears to have a more reversible character.

The picture arising from the present measurements is that these glasses undergo an initial irreversible process upon Li insertion. This is related to the disruption of some oxygen linkages in the glass network as evidenced by the DR-IR measurements, and the formation of lithium orthoborate as shown in the micro-Raman spectra. With further lithiation, there is formation of Li–O co-ordination. This process seems to be reversible, at least during the first cycle.

Earlier in situ X-ray diffraction studies [7] have not shown any alloy formation during the first cycle. There has, however been possible to discern Bragg peaks due to metallic Sn. This suggests that a reduction of  $\text{Sn}^{2+}$  to Sn is acting as charge compensation mechanism for the formation of Li–O co-ordination and ortho-phosphates, -borates.

We have earlier examined the behaviour of borate and phosphate groups in the glass network of related SnO-based glasses [7], and found similar behaviour regarding irreversible  $\text{Li}_3\text{PO}_4$  and reversible formation of Li–O during the first cycle. We also found that the borate network is more stable against disruption in an irreversible way compared to the phosphate network. Regarding the irreversibility of the  $\text{Li}_3\text{PO}_4$  formed compared to the lack of long range order  $\text{Li}_2\text{O}$ , this can be explained by considering the Gibbs free energy of formation. The formation of  $\text{Li}_3\text{PO}_4$  is favoured over  $\text{Li}_2\text{O}$  and that of  $\text{Li}_2\text{O}$  over SnO.  $\text{Li}_3\text{BO}_3$  is only formed in the absence of phosphate, and also in this case seems to be favoured over  $\text{Li}_2\text{O}$ .

#### 4. Conclusion

From the results, the following picture arises:

- The large capacity loss during the first cycle for these SnO-based glasses can partly be explained by the irreversible  $\text{Li}_3\text{BO}_3$  formation.
- The borate network is involved in the lithium insertion mechanism. Although, there is not a major disruption of the network, FT-IR measurements revealed some irreversible changes due to breakage of connections between different borate units and the disappearance of  $\text{BO}_4$  units.

## Acknowledgements

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